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Crowded organometallic compounds of the alkali metals with diphenylphosphino substituents in the organic group

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The lithium compound $[\overline{LiC(SiMe_2CH_2P}Ph_2)_3]$ **1**, obtained by metallation of the precursor $HC(SiMe_2CH_2PPh_2)_3$ **I** with LiMe, crystallised from benzene as a solvate **1**·$1.5C_6H_6$ that both in solution and in the solid state has an unusual tricyclic structure, with lithium bound to the carbanionic centre and the three phosphorus atoms. Lithiation of the related precursor $HC(SiMe_3)_2(SiMe_2CH_2PPh_2)$ **II** under similar conditions gave the dilithium compound $[\overline{Li(thf)C(SiMe_3)_2\{SiMe_2CH[Li(thf)_2]P}Ph_2\}]$ **2**, which has a fluxional structure in solution. Metallation of the precursor $HC(SiMe_3)_2(SiMe_2PPh_2)$ **III** gave the compounds $MC(SiMe_3)_2(SiMe_2PPh_2)$ (M = Li **3** or Na **4**). Compound **3** is fluxional in benzene with interchange of methyl groups between $SiMe_2$ and $SiMe_3$ fragments. Compound **4**, in contrast, has a non-fluxional molecular structure. In the solid the molecules of **4** form chains in which the sodium is bound intramolecularly to the carbanionic centre and to phenyl and intermolecularly to phenyl and phosphorus. Attempts to make the potassium analogue of **3** or **4** led to cleavage of the P–Si bond and formation of $KPPh_2$. This has a complicated polymeric crystal structure in which molecules are linked by potassium–phenyl interactions.

We have described in previous papers an extensive series of organometallic compounds containing bulky ligands of the general type $C(SiMe_3)_n(SiMe_2X)_{3-n}$ in which X is a donor group capable of co-ordinating intra- or inter-molecularly to the metal.[1] The emphasis so far has been on ligands $C(SiMe_3)_2(SiMe_2X)$ and $C(SiMe_2X)_3$ in which X = OMe,[2,3] SMe[4] or NMe_2[5,6] but we have also recently made some compounds containing the ligands $C(SiMe_3)(SiMe_2X)_2$.[7] Intramolecular M–X bonding is found in the highly unusual Grignard reagent $(Me_2\overline{NMe_2Si)_3CMg}I$,[6] which appears to have no Mg–C bond, and in the cage compounds $[\overline{LiC(SiMe_2O}Me)_2(SiMe_2X)]_2$ (X = Me[7] or OMe[3]) and intermolecular M–X bonding is found in the compounds $MC(SiMe_2NMe_2)_3$ (M = Li[6] or K[7]).

This paper describes the extension of the range of ligands to some analogous phosphorus-donor species, and the formation of the organometallic compounds $[\overline{LiC(SiMe_2CH_2P}Ph_2)_3]$ **1**, $[\overline{Li(thf)C(SiMe_3)_2\{SiMe_2CH[Li(thf)_2]P}Ph_2\}]$ **2**, $LiC(SiMe_3)_2(SiMe_2PPh_2)$ **3** and $NaC(SiMe_3)_2(SiMe_2PPh_2)$ **4**. We had previously made the tetramethylethane-1,2-diamine (tmen) complex $[Li(tmen)_2][C(SiMe_2PPh_2)_3]$ **5**, and found it to consist of separated $[Li(tmen)_2]^+$ cations and planar carbanions $[C(SiMe_2PPh_2)_3]^-$.[8a] In contrast to $LiC(SiMe_2NMe_2)_3$, the phosphorus compound does not show any interaction between the donor atom and the metal, reflecting the weaker co-ordination of the soft P towards the hard Li. Owing to the ease of cleavage of the Si–P bonds, compound **5** proved not to be useful in syntheses of derivatives of other metals so we decided to make the ligand precursor $HC(SiMe_2CH_2PPh_2)_3$ **I** in which a CH_2 group has been placed between the P and Si atoms. We now describe the structures of the product **1**, obtained by lithiation of **I**, and that of the related compound **2**, obtained by lithiation of $HC(SiMe_3)_2(SiMe_2CH_2PPh_2)$ **II**. We were unable to obtain crystals suitable for an X-ray study of the lithium derivative **3**, made by lithiation of compound $HC(SiMe_3)_2(SiMe_2PPh_2)$ **III**, but we were able to determine the structure of the sodium derivative **4**. This, together with the structure of its precursor **III**, is reported here. Attempts to make the potassium analogue of **4** led to formation of $KPPh_2$ **6**, which has a complex structure with an array of potassium–phosphorus and potassium–phenyl interactions.

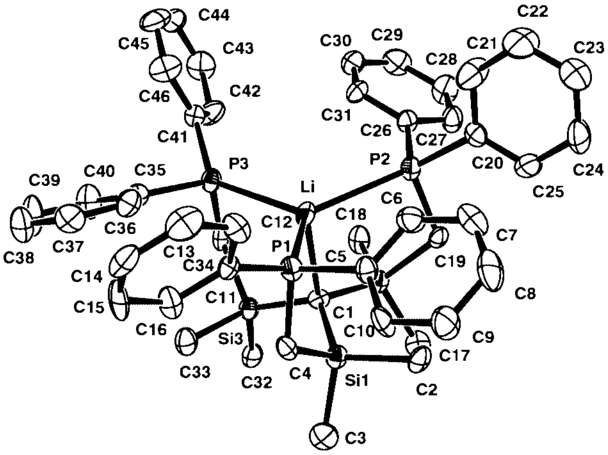

Fig. 1 Molecular structure of $[LiC(SiMe_2CH_2PPh_2)_3]$ **1**.

Results and discussion

The lithium compound 1

Compound **I** was metallated by use of MeLi in tetrahydrofuran (thf) at room temperature, but the reaction was only 70% complete and a pure bulk sample of the lithium derivative **1** was not obtained. We have not so far attempted to optimise the reaction conditions so it is possible that the yield could be improved by further work. The product was recrystallised from benzene and a crystal of **1**, taken from the mixture, was shown to have a tricyclic structure in which donor solvent is excluded from the lithium co-ordination sphere (Fig. 1). A small amount of benzene (1.5 mol per mol of **1**) was occluded in the lattice. We

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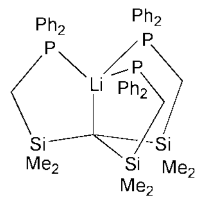
Table 1 Bond lengths (Å) and angles (°) in $LiC(SiMe_2CH_2PPh_2)_3$ **1**, $[Li(thf)C(SiMe_3)_2\{SiMe_2CH[Li(thf)_2]PPh_2\}]$ **2**, $HC(SiMe_3)_2(SiMe_2PPh_2)$ **III** and $NaC(SiMe_3)_2(SiMe_2PPh_2)$ **4**

M = Li or Na	**1**·$1.5C_6H_6$[a]	**2**[b]	**III**[c]	**4**[d]
M–C	2.222(13)	2.148(8)[e]		2.558(4)
M–P	2.652(11)	2.517(8)		3.371(2)
P–C(Ph)	1.833(7)	1.854(5)[f]	1.831(3)[f]	1.834(4)[f]
P–CH	1.813(6)	1.744(4)	—	
Si–CH	1.897(6)	1.849(4)	—	
C1–Si	1.827(6)	1.830(4)[f]	1.887(3)[f]	1.819(4)[f]
Si–Me	1.882(7)	1.886(5)[f]	1.866(3)[f]	1.875(5)[f]
P–Si			2.295(1)	2.346(2)
C–M–P	95.4(4)	101.4(3)		
Si–C1–Si	114.4(3)	115.4(2)[f]	114.4(2)[f]	116.6(2)[f]
C–Si–CH	110.5(3)	113.5(2)		
C–Si–Me	115.8(3)	114.4(2)[f]	111.7(2)[f]	114.6 [111.9(2)–116.6(2)]
Me–Si–Me	103.1(3)	99.8(2)–106.0(2)	104.0(2)–110.1(2)	104.3 [101.2(3)–106.0(3)]
P–CH–Si	113.5(3)	114.3(2)[f]		
M–C1–Si	103.9(4)	116.4(3)[g]		91.7(2), 98.9(2), 111.0(2)

[a] All values except Li–C are averages. E.s.d.s of individual measurements are given in parentheses; none differs significantly from the mean. Mean P–Li–P 119.1(4)°. [b] Li–O1 1.910(8), Li–O2 1.959(8) and Li2–O 1.915(8) Å, O1–Li–O2 107.1(4), O–Li–C10 118.2(4), O2–Li–C10 132.1(4), Li–P–C10 92.0(2), P–C10–Si3 114.3(2), Li–C1–Si3 116.4(3), O3–Li–P 116.7(4), O3–Li–C1 141.6(4), Li–C10–Si 116.49(3) and C11–P–17 96.36(19)°. [c] C1–Si–P 112.7(1), C2–Si–P 103.4(1), C3–Si–P 108.9(1), C–P–C 103.3(1), Si–P–C4 104.4(1) and Si–P–C10 98.7(1)°. [d] C1–Si–P 111.8(2), C8–Si–P 103.4(2), C9–Si–P 104.3(2), C–P–C 102.9(2), Si–P–C16 106.8(2) and Si–P–C10 99.2(2)°. [e] Value for Li–C1, Li–C10 2.151(9) Å. [f] Mean values, e.s.d.s for individual measurements in parentheses. [g] Value for Li–C10–Si, Li–C1–Si1 102.0(3), Li–C1–Si2 106.4(3) and Li–C1–Si3 99.2(3)°.

had feared that metallation of **I** might occur at a CH_2 centre as a consequence of stabilisation of the resulting carbanion by the joint action of the attached P and Si atoms [*cf.* the ready metallation of a range of phosphinomethanides,[9] and the compounds $2\text{-}Ph_2PC_6H_4CH_2SiMe_3$ and $\{Ph_2(Me_3SiN{=})P\}_2CH_2$[10]]. The observed preferential metallation of **I** at the central quaternary carbon may be due not to a greater acidity of the H at that centre but to the very effective internal solvation of the Li atom there. A solution of **1** in thf-d_8 showed a 1 : 1 : 1 : 1 quartet ($^1J_{LiP}$ = 44 Hz) in the ^{31}P NMR spectrum and a 1 : 3 : 3 : 1 quartet in the ^7Li spectrum, indicating that the co-ordination of the three P atoms to Li persists even in the oxygen-donor solvent and pointing to the remarkable stability of the tricyclic species. Moreover, compound **1** is obtained exclusively even when the lithiation of $HC(SiMe_2CH_2PPh_2)_3$ is carried out in benzene containing a tenfold excess of tmen. In contrast, the lithium phosphinomethanides are obtained as solvent-free complexes only when they are prepared in hydrocarbon media.[9]



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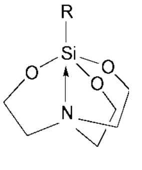

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The anionic ligand in compound **1** shows a close skeletal resemblance to the trianionic tripodal ligands in metallatranes such as the silatranes $R\overline{Si(OCH_2CH_2)_3N}$ **7**, but the co-ordination to the metal centre is provided by the lone pair of electrons of the carbanion rather than by that of the nitrogen atom. The propeller-shaped lithium derivative has no crystallographic symmetry but there is an approximate C_3 axis along the Li–C bond and the Si_3 and P_3 planes are parallel. None of the chemically equivalent bond lengths or angles differs significantly from the mean values given in Table 1. The Li–C [2.222(13) Å] and mean Li–P bond lengths are in the normal range for phosphinomethanides[9] suggesting that the structure of **1** is remarkably strain-free. The mean C–Li–P angle (95.4°) is considerably less than the tetrahedral angle but ligation of lithium by solvent is prevented by the preferential ligation of the PPh_2 groups of the ligand, which completes the lithium co-ordination sphere. The P–CH_2 bonds are shorter than the P–Ph bonds as expected,[9,10a] but, in contrast to data for lithium phophinomethanides, the Si–CH_2 [1.897(6) Å] is similar to the Si–Me bond length [1.882(7) Å]. The Si–C(1) bonds [1.827(6) Å] are shorter, suggesting that, as in similar species,[11] the carbanionic charge is delocalised mainly within the CSi_3 core. Although this is not planar as in **5**, the mean Si–C–Si angle (114.4°) is significantly greater than the tetrahedral value.

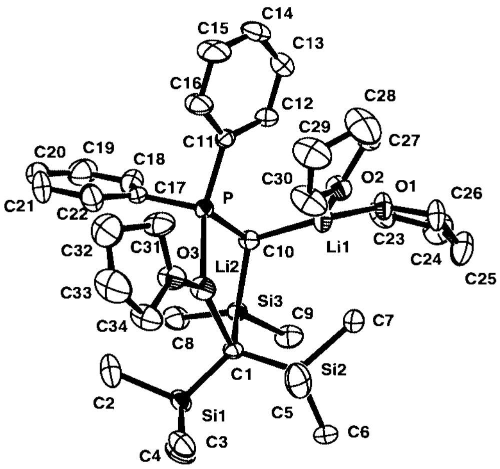


Fig. 2 Molecular structure of $[Li(thf)C(SiMe_3)_2\{SiMe_2CH[Li(thf)_2]PPh_2\}]$ **2**.

The dilithium compound 2

In order to examine the effect of co-ordination of lithium by only one phosphorus centre we made the precursor $HC(SiMe_3)_2(SiMe_2CH_2PPh_2)$ **II**. When this was treated with methyllithium in 1 : 1 molar proportion unchanged **II** was recovered together with the dilithium species **2**, which could be made quantitatively by treating **II** with two equivalents of LiMe. The structure of **2** is shown in Fig. 2; the lithium atom Li2 is bound to the Si_3-stabilised carbanionic centre C1 and the atom Li1 to the P,Si-stabilised centre C10. In the light of the isolation of **1**, in which there is clean lithiation at only one of the potential sites, the formation of the dilithium species **2** is surprising. The absence of any detectable monolithium species indicates that lithiation at the CH centre facilitates attack at the CH_2 group, which is probably activated by the co-ordination of the adjacent phosphorus to lithium. It is possible that the effect in the monolithium derivative of **II** is greater than that in **1** because the single phosphorus can co-ordinate to Li more strongly than an individual phosphorus atom in **1**, which has to compete with two others. The strong co-ordination persists in the dilithium compound **2** as shown by the Li–P bond length [2.517(8) Å *cf.* 2.652(11) Å in **1**]. We attempted to generate the monolithiated species by treatment of **2** with a stoichiometric quantity of $[NHMe_3]Cl$ or phenol but were not able to isolate a clean product.

Bond lengths and angles for compound **2** are given in Table 1. The Li–C bond lengths are at the short end of the usual range,[12] but similar to those in $Li(pmdta)CH(SiMe_3)_2$ [2.13(5) Å],[13] $[LiC(SiMe_3)_2PMe_2]_2$ [2.172(4) Å],[9] or $[Li(tmen)CH_2PR_2]_2$ [2.141(6)–2.174(6) Å] [$R_2 = Me_2$, Ph_2 or PhMe, pmdta = $Me_2N(CH_2)_2NMe(CH_2)_2NMe_2$].[10a,14a] The C1–Si [mean 1.830(4) Å] and C10–Si bonds [1.849(4) Å] are short and the Si–C1–Si angles [114.3(2)–116.9(2)°] are all much wider than the tetrahedral value, as in **1** and the related compounds $LiC(SiMe_3)_2(SiMe_2X)$ (X = OMe[2] or NMe_2[5]) where there is delocalisation of charge from carbon to silicon. The Li–P bond length is similar to those in phosphanides that contain three-co-ordinate Li, *e.g.* $LiPPh_2{\cdot}OEt_2$ [2.483–2.496(10) Å],[14b] $[LiC(SiMe_3)_2PMe_2]_2$ [2.519(4) Å],[9b] and a fluorophosphanide [2.517(6) Å].[14c] The configuration at Li2 is planar and that at Li1 nearly so (sum of angles 357.4°). In the 5-membered chelate ring each of the atoms P, Li2, C1 and Si3 is displaced slightly and the atom C10 considerably from the mean plane. As in **1** the P–CH_2 are much shorter than the P–Ph bonds.

The ^1H, ^7Li, ^{13}C, ^{29}Si and ^{31}P NMR spectra of compound **2** in toluene-d_8 at 182 K suggest that at this temperature the structure found in the crystal is present also in solution. The resonances in the ^{13}C spectrum attributed to the carbon atoms C1 and C10 were located by INEPT (insensitive nuclei enhanced by polarisation transfer) and DEPT90 pulse sequences. The resonance ascribed to the proton attached to C10 was identified by nuclear Overhauser effect measurements. Irradiation of the protons attached to *ortho*-hydrogen atoms of the phenyl groups (C12, C16, C18 and C22) and those attached to the α-hydrogen atoms of the thf (C23, C26, C27, C30, C31 and C34) significantly enhanced the signal from the C10 proton, whereas irradiation at other positions gave only weak (C8 and C9) or no enhancement.

As the sample was allowed to warm to 193 K the resonances ascribed to the protons attached to the carbon atoms C12 and C16 merged with those ascribed to the protons attached to C18 and C22, indicating that the two phenyl groups were exchanging positions rapidly on the NMR timescale with $\Delta G^{\ddagger} = 39$ kJ mol^{-1}. At this temperature the resonance of the atom Li2 in the ^7Li spectrum was a doublet ($^1J_{LiP} = 44$ Hz, *cf.* 45 Hz for **1** and 48.5 Hz for $LiN(SiMe_2CH_2PPr^i{}_2)_2$[15]), showing that the Li2–P bond was intact. At higher temperatures the doublet ascribed to Li2 became a singlet and at 271 K the signals from the two lithium atoms merged. A value of $\Delta G^{\ddagger} = 50$ kJ mol^{-1} was calculated for the exchange process. These results can be rationalised if there is a significant electrostatic (*i.e.* non-localised) component in the bonding between the lithium centres in **2** and the bulky carbanionic $[C(SiMe_3)_2\{SiMe_2CHPPh_2\}]$ group (*cf.* crystals of the alkali metal derivatives of aromatic hydrocarbons[16a,b]). If the structure of **2**, as determined by the X-ray study, is preserved in solution, within a solvent cage, it is possible to envisage that, as the temperature is raised, the lithium–carbanion bonding weakens in two stages. The process with the lower activation energy leads to inversion at the carbanionic centre C10 (we have recently described inversions at similar centres[17]) and the process with slightly higher activation energy involves interchange of (thf-solvated) Li between the two carbanionic sites in the $[C(SiMe_3)_2\{SiMe_2CHPPh_2\}]$ fragment.

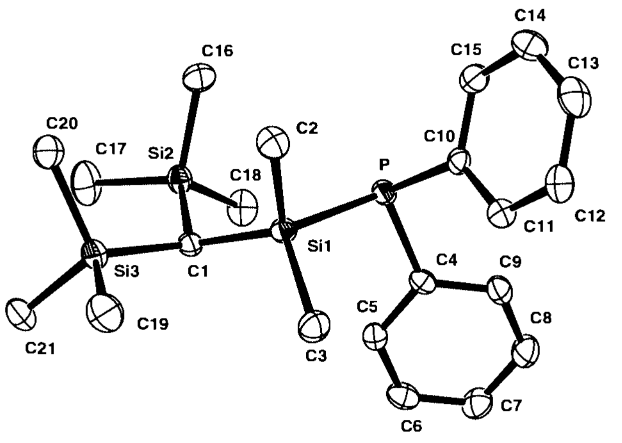
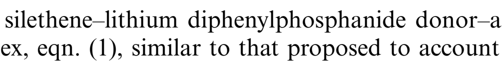


Fig. 3 Molecular structure of $HC(SiMe_3)_2(SiMe_2PPh_2)$ **III**.

Compounds containing the ligand $C(SiMe_3)_2(SiMe_2PPh_2)$

The structure of $HC(SiMe_3)_2(SiMe_2PPh_2)$ **III** (Fig. 3) requires little comment. There is considerable variation in chemically equivalent bond lengths and angles but, for the most part, the mean values are similar to those in the related compound $HC(SiMe_2PPh_2)_3$ **IV**.[8] The P–Si bond length [2.295(1) Å] is longer than that in **IV** [2.275(1) Å]. The Me2–Si–Me3 angle [110.1(2)°] is also remarkably wide (*cf.* the mean for the other Me–Si–Me angles in **III** 106.8 and **IV** 106.0°).

Compound **III** reacts with methyllithium to give the organolithium compound **3**. This may be isolated from toluene–hexane as large yellow crystals suggesting that the species in the solid state is well defined, but, in spite of numerous attempts, we have been unable to obtain a sample suitable for an X-ray study. Owing to the extreme air- and moisture-sensitivity of the compound we have not been able to obtain a satisfactory C and H analysis but the ^1H NMR spectrum at room temperature is consistent with the composition $[Li(thf)_nC(SiMe_3)_2(SiMe_2PPh_2)]$ ($n = 2$ or 3). The ^1H, ^7Li and ^{29}Si NMR spectra of samples in the temperature range 248–343 K indicate that the species in solution undergo a series of reversible concentration-dependent changes reminiscent of those observed for $Li(thf)_2C(SiMe_3)_3$ or other organolithium compounds (*e.g.* LiPh) which have thoroughly been investigated.[18,19] At 338 K the ^1H, ^{13}C and ^{29}Si signals assigned to the distinct $SiMe_2$ and $SiMe_3$ groups give single sharp peaks showing that there is interchange between methyl and PPh_2 groups attached to silicon. There is no evidence for coupling between the P and the Si, C, or H nuclei, but both the ^{31}P and ^7Li signals are broad, possibly due to unresolved Li–P coupling as well as quadrupolar relaxation. The NMR spectra at 338 K can be interpreted in terms of the reversible formation of a solvent-caged silethene–lithium diphenylphosphanide donor–acceptor complex, eqn. (1), similar to that proposed to account for the chemistry of the compounds $MC(SiMe_3)_2(SiPh_2X)$ (M = Li or Na; X = F or Br).[20a] Scrambling of organic groups between SiR_2 and SiR_3 fragments could proceed through the silethene **8**[20b] but it is not possible to ascertain whether the methyl transfer is concerted over the CSi_3 system. Alternatively, a methyl group could migrate from $SiMe_3$ to a positive Si centre (*cf.* ref. 20*c*) formed by transfer of PPh_2^- to lithium without breaking the Li–C bond. Further work is required to understand the complex equilibria between species (possibly involving oligomers



$$LiC(SiMe_3)_2(SiMe_2PPh_2) \rightleftharpoons \begin{bmatrix} (Me_3Si)_2C{=}SiMe_2 \\ Li{-}PPh_2 \end{bmatrix} \qquad (1)$$

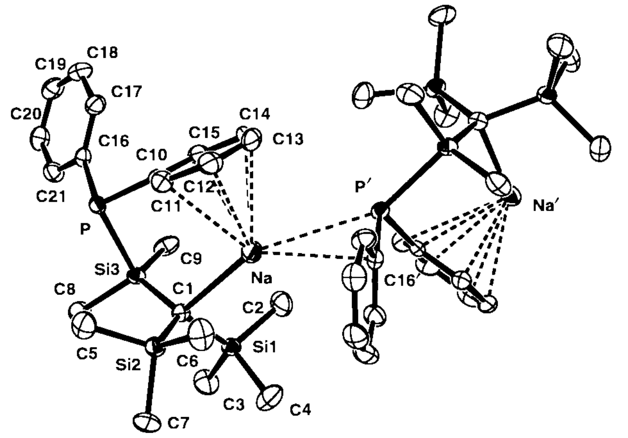
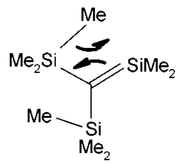


Fig. 4 Structure of $NaC(SiMe_3)_2(SiMe_2PPh_2)$ **4**.



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and ate complexes) evident from the NMR spectra obtained from **3** at low temperatures.

Although we could not determine the structure of compound **3** we were able to isolate the corresponding sodium derivative **4**. This was readily made in 55% yield by treatment of **III** with sodium *tert*-butoxide and methyllithium in thf, and in higher yield, but less conveniently, from **III** and methylsodium. The crystals obtained from pentane were sufficiently air-sensitive to preclude satisfactory C and H analysis but were more easily handled than those of **3**. Their identity was confirmed by an X-ray structural determination which indicated that they were solvent-free. The structure is shown in Fig. 4 and bond lengths and angles are given in Table 1. The lattice consists essentially of monomers in which each sodium is co-ordinated to the central carbanion and to a phenyl group, with Na–C distances similar to those in numerous other organometallic compounds.[16a] The sodium atoms interact more weakly with phosphorus atoms (Na–P 3.371(2) Å, *cf.* 2.883(8) and 2.936(7) Å in $[Na(pmdeta)\{PH(C_6H_{11})\}]_2$[21a]), and with *ipso*-carbon atoms of phenyl groups in neighbouring molecules, to give chains along the screw axis parallel to *b*. Table 1 shows that the P–C, C1–Si and Si–Me bond lengths are similar to those in **1**–**3**, but the P–Si bond length [2.346(2) Å] is unusually long, perhaps as a consequence of the delocalisation of carbanionic charge on to silicon [*cf.* P–Si 2.275(2) Å in $HC(SiMe_2PPh_2)_3$ **IV**, 2.323(3) Å in $[Li(tmen)_2][C(SiMe_2PPh_2)_3]$,[8] 2.266(4) Å in $Zr(Cp)_2P_6(SiMe_3)_4$,[21b] 2.17 Å in $[Li(tmen)_2][P(SiH_3)_2]$,[21c] 2.110(8)–2.2146(7) Å in $P(SiMe_3)_2$ derivatives[21d] and 2.24–2.29 Å in most organosilylphosphines[21e]]. The Si–C1–Si, Me–Si–Me, C1–Si–Me and C1–Si–P angles are all in the usual range; average values are given in Table 1 since none of the individual measurements differs significantly from the mean. The Si3–P–C10 angle [99.2(1)°] is narrower than the tetrahedral value presumably because the phenyl group C10–C15 is pulled towards the sodium. The Na···C6 and Na···C2 distances are short but not unusually so;[16] the methyl groups show no distortion from tetrahedral geometry and thus there is no indication of a bonding interaction with the metal.

Compound **4** dissolves in both aromatic and aliphatic hydrocarbons, indicating that the weak intermolecular Na···P and Na···Ph interactions are broken upon dissolution. In the NMR spectra (in C_6D_6) each of the ^1H, ^{13}C and ^{29}Si resonances of the $C(SiMe_3)_2SiMe_2$ fragment shows coupling to phosphorus so that, in contrast to the situation for **3**, there is no evidence that the P–Si bonds are broken. It appears that the molecular units found in the crystal are retained in solution.

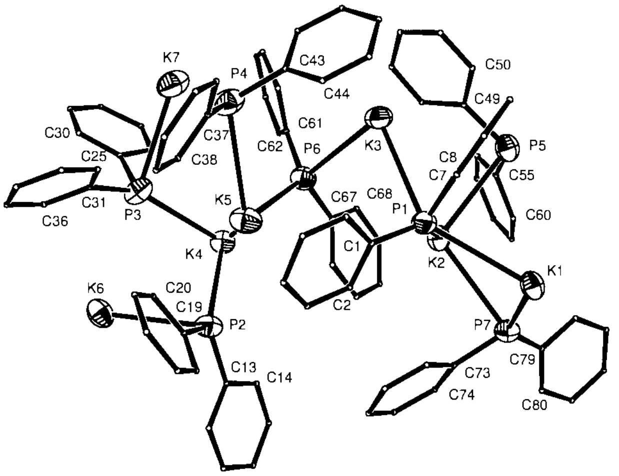

Fig. 5 The asymmetric unit in $KPPh_2$ **6**.

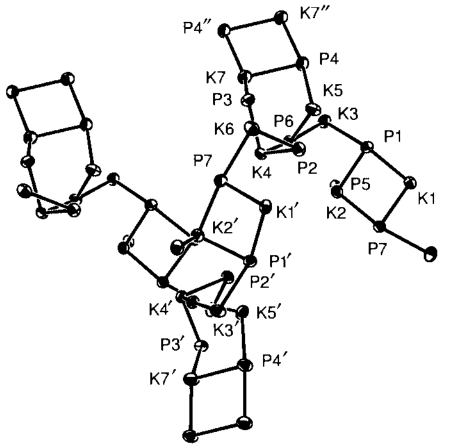

Fig. 6 The K–P framework in compound **6**.

Reactions between compound **3** and potassium *tert*-butoxide or between **III** and methylpotassium in thf at room temperature gave an orange solution. The solvent was removed, the residual solid washed with hexane then dissolved in hot toluene (*ca.* 50 °C). When this solution was allowed to cool orange crystals separated and a structure determination showed that they were of potassium diphenylphosphanide $KPPh_2$, **6**. This could be formed by direct replacement of lithium in the $LiPPh_2$ shown on the right of eqn. (1) or from a potassium analogue of **4**, which is unstable in solution. We have not isolated the silicon-containing compound but assume it to be the dimer of **8**, $[(Me_3Si)_2\overline{CSiMe_2C(SiMe_3)_2S}iMe_2]$,[22] which is a common decomposition product of alkali metal compounds containing organosilyl-substituted carbanions $C(SiMe_3)_2(SiMe_2X)$ in which X is a good leaving group.[20a] The disilacyclobutane would have been discarded in the hexane washings during work-up.

The structure of $KPPh_2$

Since the crystal structure of $KPPh_2$ had not apparently been described we decided to refine our data. The structure is exceedingly complicated with seven molecules in the asymmetric unit shown in Fig. 5. In order to describe the K–P framework it is necessary to set arbitrary upper limits for the lengths of constituent bonds. Interactions with K–P <3.5 Å are shown in Fig. 6 which indicates that 4-membered K1P7K2P1 and 6-membered K4P6K5P4K7P3 rings are linked by K3 which bridges P1 and P6 and by K6P2 which link P7 and K4. The

Table 2 Bond lengths in $KPPh_2$ **6**

K1–P7 3.3232(13), K1–P1 3.4142(13)	K1–C	η^5 3.086(4)–3.334(4); η^5 3.138(4)–3.315(4)
K2–P1 3.2585(13), K2–P7 3.3386(13), K2–P5 3.3459(14)	K2–C	η^6 3.186(4)–3.278(2); η^2 3.251(4), 3.302(3)
K3–P6 3.3281(14), K3–P1 3.3350(13)	K3–C	η^2 3.199(4), 3.337(4); η^4 3.279(5)–3.413(4) η^4 3.284(5)–3.390(5)
K4–P2 3.2062(13), K4–P3 3.2291(14)	K4–C	η^6 3.086(4)–3.290(4); η^2 3.335(3), 3.382(4)
K5–P6 3.2615(14), K5–P4 3.4019(15)	K5–C	η^4 3.132(5)–3.494(4); η^1 3.316(4)
K6–P2 3.3205(15), K6–P7′ 3.4352(14),	K6–C	η^2 3.118(4), 3.189(3); η^2 3.163(4), 3.218(4)
K7–P3 3.2430(17), K7–P4″ 3.2831(15), K7–P4 3.4949(16)	K7–C	η^2 3.077(4), 3.385(5); η^2 3.168(5), 3.238(7) η^1 3.385(5); η^1 3.446(4)

Symmetry transformations: ′ $3 - x, y - \frac{1}{2}, -z + \frac{1}{2}$; ″ $-x, -y, -z$.

asymmetric units are linked into helices about the 2_1 screw axis of the space group and the helices are linked by inversions at the centres of the $(P4K7)_2$ rings. The 4-membered rings linking the asymmetric units are reminiscent of those in the ladder structures of *e.g.* $KPHC_6H_3(C_6H_2Me_3\text{-}2,4,6)_2\text{-}2,6$ **9** or $K(thf)P(SiMe_3)_2$[21d] or lithium phosphanides such as $[Li_2(\mu_3\text{-}Bu^t{}_2P)(\mu\text{-}Bu^t{}_2P)(thf)]_2$, or $[LiP(SiMe_3)_2]_6$.[24] Helical structures have been found in $Li\{Me(OCH_2CH_2)_2OMe\}PHMe$.[24c] Each phosphorus interacts strongly with two or three potassium atoms and the framework is held together by further, slightly weaker, interactions between phosphorus and potassium neighbours. The co-ordination sphere round potassium is completed by potassium–phenyl interactions. Those which give K–C <3.5 Å are listed in Table 2; the range of hapticities (η^{1-2} or η^{4-6}) is noteworthy and reflects the complexity of the K–P framework. The K–P bond lengths [3.2062(13)–3.4949(16) Å] are in the range associated with electrostatic interactions[25] in a number of other phosphanides, *e.g.* 3.043(2)–3.438 in **9**, 3.497(4) in $[Cp_2ZrHP(C_6H_2Bu^t{}_3\text{-}2,4,6)K(thf)_2]$,[25] 3.306(2)–3.669(1) in $K_3(thf)_2(PHC_6H_2Me_3\text{-}2,4,6)_3$,[26] 3.251(2)–3.658(3) in $[K(pmdta)\{(Bu^tP)_2H\}]$[27] and 3.256(1)–3.264(1) Å in phosphole derivatives.[28] Potassium–phenyl interactions have now been documented in a wide range of organometallic derivatives,[16] including a number of phosphanides.[23,25] Individual K–C distances in **6** differ significantly from each other but it appears that (*a*) for η^5- and η^6-co-ordinated Ph groups the bond distances are shortest (*ca.* 3.2 Å), (*b*) for η^1- and η^4-co-ordinated groups the distances are longer (3.5–3.6 Å) and (*c*) for η^2-co-ordinated groups the distances are very variable. These generalisations are consistent with data tabulated previously.[16a]

Conclusions

We have concentrated in this paper on describing the syntheses and structures of the alkali metal derivatives derived from the diphenylphosphino ligand precursors **I**–**III**, but it seems appropriate to consider briefly their potential as ligand transfer reagents for the syntheses of further organometallic compounds. The ligand $C(SiMe_2CH_2PPh_2)_3$ has the most potential for the development of further chemistry and we know of no other strain-free tetradentate ligand containing a hard carbanionic centre and three soft phosphorus centres, though ligands containing one silicon and three phosphorus or nitrogen centres have been described.[29] Compound **1** should be particularly valuable in making derivatives of later transition metals but its stability indicates that derivatives of other hard metals should be accessible also.

The other ligands discussed here have less potential. The precursor $HC(SiMe_3)_2(SiMe_2CH_2PPh_2)$ **II** reacts with LiMe at both CH and CH_2 centres, making subsequent synthetic procedures complicated, and the ligand $C(SiMe_3)_2(SiMe_2PPh_2)$, like $C(SiMe_2PPh_2)_3$,[8] is easily cleaved at Si–P bonds. Reactions of compound **3** with a number of metal halides gave complex mixtures containing a variety of phosphorus compounds similar to those formed from reactions of **5** with metal halides.[8] Nevertheless the lithium, sodium and potassium compounds described here show an interesting and varied range of chemistry. The lithium compound is markedly more air-sensitive and the potassium compound much more thermally unstable than the sodium analogue, which dissolves in hydrocarbons to give stable molecular species. That **3** is more air-sensitive than **4** may perhaps be because attack at the sodium centre is slowed down by the intramolecular co-ordination of phenyl groups.

The fluxional properties of the lithium compound **3** are not surprising in view of previous work,[20] but it is noteworthy that a similar behaviour is not observed with **4**. It is possible that co-ordination of phenyl may push the phosphorus away from the sodium to make intramolecular elimination of $NaPPh_2$ more difficult. In contrast, elimination of $KPPh_2$ from the potassium analogue of **3** or **4** appears to be extremely facile. The process takes place in thf so the species formed are probably $KPPh_2$ solvates or oligomers like those found for $LiPPh_2$,[14b,30] but it is not possible to discern whether the K–P bonds are formed intra- or inter-molecularly. The $K \cdots P$, $K \cdots Ph$ and $K \cdots O$ interactions appear to be of similar strength so that the balance between them is a subtle one. When the thf solution of $KPPh_2$ is concentrated the $K \cdots P$ and $K \cdots Ph$ interactions are sufficiently strong to exclude thf from the crystalline solid that separates. This is in contrast to the behaviour of $LiPPh_2$, which crystallises from Et_2O or thf as an ether solvate.[14b]

Experimental

Air and moisture were excluded as far as possible by the use of Schlenk techniques and Ar as blanket gas. Glassware was flame-dried under vacuum and solvents were dried and distilled immediately before use. NMR spectra were recorded at 500.1 (^1H), 125.6 (^{13}C), 194.5 (^7Li), 99.4 (^{29}Si) and 202.4 (^{31}P) MHz and chemical shifts are given relative to $SiMe_4$ for H, C and Si, aqueous LiCl for Li, and H_3PO_4 for P. Except where indicated solutions in C_6D_6 at 298 K were used.

Preparations

Tris[(diphenylphosphinomethyl)dimethylsilyl]methane I. A solution of $HC(SiMe_2Br)_3$[31] (1.75 g, 4.1 mmol) in benzene (40 cm^3) was added at room temperature to a suspension of $LiCH_2PPh_2\cdot tmen$ (5.9 g, 18 mmol)[32] in benzene (40 cm^3). When the solution became clear the solvent was pumped off to leave a white solid, which was crystallised from hexanes to give $HC(SiMe_2CH_2PPh_2)_3$ **I** as a white solid (2.22 g, 69%) (Found: C, 66.7; H, 7.0; P, 11.2. $C_{46}H_{55}P_3Si_3$ requires C, 70.4; H, 7.1; P, 11.8%). In spite of the low C analysis, no impurities were detected by NMR spectroscopy: δ_H (thf-d_8) −0.15 (1 H, s, CH), 0.00 (18 H, s, $SiMe_2$), 1.47 (2 H, s, CH_2), 7.23–7.30 and 7.41–7.45 (30 H, m, Ph). δ_C 3.2 (d, $^2J_{CP} = 5.4$, $SiMe_2$), 4.7 (q, $^3J_{PC} = 43$, CH), 17.8 (d, $^1J_{CP} = 31.9$, CH_2), 128.8 (d, $^3J_{CP} = 3$, *m*-C), 128.9 (s, *p*-C), 133.0 (d, $^2J_{PC} = 20$, *o*-C) and 142.3 (d, $^1J_{CP} = 18.8$ Hz, *ipso*-C). δ_P −17.4. *m/z* 784 (20, *M*), 769 (5, *M* − Me), 707 (30, *M* − Ph) and 585 (100%, *M* − Ph_2PCH_2).

Tris[(diphenylphosphinomethyl)dimethylsilyl]methyllithium 1. A solution of LiMe (9.6 mmol) in Et_2O (0.6 cm^3) was added to a solution of compound **I** (0.61 g, 7.7 mmol) in thf at room temperature. The mixture was stirred overnight to give a solution shown by NMR spectroscopy to contain **I** (34%) and the lithium compound **1** (66%). δ_H (thf-d_8) 0.28 (18 H, s, SiMe$_2$), 1.61 (6 H, d, $^2J_{PH}$ = 6.6 Hz, CH$_2$), 6.83–7.05 and 7.39–7.44 (m, Ph). δ_C (C$_6$D$_6$) 7.1 (s, SiMe$_2$), 30.1 (s, CH$_2$), 128.6 (d, Ph), 133.0 (d, $^2J_{PC}$ = 7.2 Hz, *o*-C) and 140.0 (*ipso*-C). δ_{Li} 4.2 (q, $^1J_{LiP}$ = 45 Hz). δ_P –13.0 (q, $^1J_{LiP}$ = 44.7 Hz). The solvent was pumped off to leave a white solid mixture of **I** and **1**, which was recrystallised from benzene. A single crystal of **1** was extracted for an X-ray study.

{(Diphenylphosphinomethyl)dimethylsilyl}bis(trimethylsilyl)methane II. A solution of HC(SiMe$_3$)$_2$(SiMe$_2$Br) (3.88 g, 1.30 mmol) in thf (20 cm^3) was added at room temperature to a stirred solution of Li(tmen)CH$_2$PPh$_2$ (4.20 g, 1.30 mmol) in thf (15 cm^3). The yellow solution was stirred for 48 h, and solvent removed to leave a sticky solid, which was extracted with pentane (2 × 30 cm^3). The solvent was removed from the extract and the residue distilled at 145–148 °C at 10^{-3} Torr to give compound **II** as a colourless oil (3.8 g, 70%) (Found: C, 63.3; H, 9.0. C$_{22}$H$_{37}$PSi$_3$ requires C, 63.4; H, 9.0%). δ_H −0.59 (1 H, s, CH), 0.14 (18 H, s, SiMe$_3$), 0.16 (6 H, s, SiMe$_2$), 1.44 (2 H, s, CH$_2$), 7.10 (6 H, m, *m*- and *p*-H) and 7.51 (4 H, t, *o*-H). δ_C 3.0 (d, $^3J_{CP}$ = 5.2, SiMe$_2$), 3.3 (s, Si$_3$C), 3.5 (s, SiMe$_3$), 17.3 (d, $^1J_{CP}$ = 31.7, CH$_2$), 128.5 (d, $^3J_{CP}$ = 2.3 Hz, *m*-C), 128.6 (s, *p*-C), 133.2 (d, $^2J_{PC}$ = 19.8, *o*-C) and 142.0 (d, $^1J_{CP}$ = 15.9 Hz, *ipso*-C). δ_P −16.7. *m/z* 416 (30, *M*), 401 (25, *M* − Me), 381 (15, *M* − 2Me), 325 (15), 293 (20), 217 (100), 200 (80), 183 (55), 129 (50) and 73 (80%).

Li(thf){C(SiMe$_3$)$_2$[SiMe$_2$CHLi(thf)$_2$PPh$_2$]} 2. A solution of compound **II** (0.78 g, 1.88 mmol) in thf (20 cm^3) was treated with LiMe (1.88 mmol) in thf (10 cm^3) at −78 °C and the pale yellow solution allowed to warm to room temperature. The solvent was removed to leave a sticky glass, from which unchanged **II** was removed by washing with cold pentane (2 × 10 cm^3, 0 °C). The residual solid was recrystallised from toluene at −30 °C to give pale yellow blocks of **2**, suitable for an X-ray study (0.29 g. 57% based on LiMe), mp 120–125 °C (softens 80 °C). The yield of **2** can be increased to *ca.* 90% by using 2LiMe/**II** stoichiometry (Found: C, 62.8; H, 9.0. C$_{34}$H$_{59}$Li$_2$O$_3$PSi$_3$ requires C, 63.3; H, 9.2%). δ_H (toluene-d_8, 182 K) 0.24 (1 H, d, $^2J_{PH}$ = 25 Hz, CH), 0.78 (6 H, s, SiMe$_2$), 0.85 (18 H, s, SiMe$_3$), 1.04 (12 H, s, thf), 3.15 (12 H, s, thf), 6.94–7.31 (6 H, m, Ph), 7.65 and 7.77 (2 H, s, *o*-H). δ_C 3.2 (s, CSi$_3$), 8.1 (s, SiMe$_3$), 11.4 (d, $^3J_{PC}$ = 6.5, SiMe$_2$), 17.3 (d, $^1J_{PC}$ = 25 Hz, CH), 25.3 (s, thf), 68.2 (s, thf), 126.2 (s, *p*-C), 128.0 (d, $^3J_{PC}$ = 6.2, *m*-C), 131.7 (d, $^2J_{PC}$ = 15.8, *o*-C) and 151.9 (d, $^1J_{PC}$ = 3.8 Hz, *ipso*-C). δ_{Li} (toluene-d_8, 223 K) 0.47 (s, Li1) and 2.83 (d, $^1J_{LiP}$ 44 Hz, Li2). δ_{Si} −11.7 (s, SiMe$_3$) and −10.2 (d, $^2J_{PSi}$ = 46.1 Hz). δ_P 1.6 (br q, $^1J_{LiP}$ = *ca.* 48 Hz).

[(Diphenylphosphino)dimethylsilyl]bis(trimethylsilyl)methane III. A solution of KPPh$_2$ (59.0 mmol) in thf (120 cm^3) was added dropwise at room temperature to a stirred solution of HC(SiMe$_3$)$_2$(SiMe$_2$Br) (17.6 g, 59.2 mmol) in thf (60 cm^3). The solvent was removed under vacuum to leave a yellow solid which was extracted with hexane (2 × 100 cm^3) and the extract filtered to remove KBr. The solvent was evaporated from the filtrate to give a paste, which on standing at room temperature for one week gave pale yellow crystals of **III** (22 g, 93%), mp 60–61 °C (Found: C, 62.3; H, 8.5. C$_{21}$H$_{35}$PSi$_3$ requires C, 62.6; H, 8.6%). δ_H −0.52 (1 H, s, CH), 0.19 (18 H, s, SiMe$_3$), 0.31 (6 H, d, $^3J_{PH}$ = 3.3, SiMe$_2$), 7.08 (6 H, m, *m*-, *p*-H) and 7.52 (4 H, t, *J* = 9 Hz, *o*-H). δ_C 1.1 (d, $^2J_{CP}$ = 8.9, SiMe$_2$), 2.8 (d, $^2J_{CP}$ = 11.4, CSi$_3$), 3.7 (d, $^2J_{CP}$ = 3.3, SiMe$_3$), 127.8 (*p*-C), 128.6 (d, $^3J_{CP}$ = 6.4, *m*-C), 134.3 (d, $^2J_{CP}$ = 17.4, *o*-C) and 137.1 (*ipso*-C, $^1J_{CP}$ = 19.1 Hz). δ_{Si} −0.1 (d, $^3J_{SiP}$ = 4.2, SiMe$_3$) and 2.5 (d, $^1J_{SiP}$ = 27.5 Hz, SiMe$_2$). δ_P −46.9. *m/z* 402 (30, *M*), 387 (45, *M* − Me), 217 [100, (Me$_3$Si)$_2$C=SiMe$_2$], 201 [25, Me$_2$SiC(SiMe$_3$)SiMe$_2$], 186 (35, PPh$_2$), 129 (75), 108 (40, PPh) and 73 (75%, SiMe$_3$).

Li(thf)$_2$C(SiMe$_3$)$_2$(SiMe$_2$PPh$_2$) 3. A solution of LiMe (3.28 mmol) in thf (10 cm^3) was added to a solution of compound **III** (1.23 g, 3.28 mmol) in thf (20 cm^3) at room temperature, and the yellow solution then stirred for 3 h and the solvent removed under vacuum to leave a dark yellow paste. This was dissolved in toluene (5 cm^3) and the solution carefully layered with hexane, to give large yellow crystals (1.26 g, 75%), mp 88 °C (Found: C, 57.7; H, 9.6. C$_{21}$H$_{34}$LiPSi$_3$·2C$_4$H$_8$O requires C, 63.0, H, 9.1%). δ_H 0.48 (18 H, s, SiMe$_3$), 0.70 (6 H, s, SiMe$_2$), 1.33 (8 H, m, thf), 3.34 (8 H, m, thf), 6.91–7.15 (6 H, m, Ph) and 7.68–7.72 (4 H, m, *o*-H). δ_C 7.0 (s, SiMe$_3$), 8.4 (s, SiMe$_2$), 25.3 (s, thf), 68.4 (s, thf), 122.7 (s, *p*-C), 128.1 (d, $^3J_{PC}$ = 5.8, *m*-C), 131.6 (d, $^2J_{PC}$ = 15.7) and 149.6 (d, $^1J_{PC}$ = 31.4 Hz, *ipso*-C). δ_{Li} 0.89. δ_{Si} −10.2 (SiMe$_3$) and −10.0 (SiMe$_2$). δ_P −38.9. The ^{1}H, ^{13}C and ^{29}Si signals assigned to SiMe$_2$ and SiMe$_3$ groups merge as the sample is heated from 305 to 338 K.

NaC(SiMe$_3$)$_2$(SiMe$_2$PPh$_2$) 4. A solution of LiMe (4.27 mmol) in thf (10 cm^3) was added at room temperature to a solution of compound **III** (1.72 g, 4.27 mmol) and NaOBu^t (0.41 g, 4.27 mmol) in thf (20 cm^3). The cloudy orange mixture was stirred for 14 h and the solvent then pumped off to give a sticky residue, which was extracted with pentane (20 cm^3). The extract was filtered to remove a small amount of solid. Some solvent was removed from the filtrate and slow cooling gave large pale yellow crystals (1.0 g, 55%), mp 125 °C (decomp.) (Found: C, 57.1; H, 8.1. C$_{21}$H$_{34}$NaPSi$_3$ requires C, 59.4; H, 8.1%). No impurities were detected by NMR spectroscopy. δ_H 0.30 (18 H, s, SiMe$_3$), 0.57 (6 H, d, SiMe$_2$, $^3J_{PH}$ = 3.6 Hz), 6.91–7.08 (6 H, m, *m*- and *p*-H) and 7.57 (4 H, m, *o*-H). δ_C 2.8 ($^2J_{PC}$ = 24.1, $^1J_{SiC}$ = 75.6, CSi$_3$), 6.2 ($^2J_{PC}$ = 17.5, SiMe$_2$), 8.4 ($^4J_{PC}$ = 3.3, $^1J_{SiC}$ = 56.0, SiMe$_3$), 126.7 (*p*-C), 128.3 ($^3J_{PC}$ = 6.4, *m*-C), 134.4 ($^2J_{PC}$ = 15.9, *o*-C) and 141.4 ($^1J_{PC}$ = 22.8 Hz, *ipso*-C). δ_{Si} −10.6 ($^3J_{PSi}$ = 3.7, SiMe$_3$) and −2.2 ($^1J_{PSi}$ = 26.1 Hz, SiMe$_2$). δ_P −38.6. *m/z* 424 (75, *M*), 402 [60, RH, R = C(SiMe$_3$)$_2$(SiMePPh$_2$)], 386 (70, R − Me), 217 (R − PPh$_2$, 95), 201 (100), 185 (60, PPh$_2$), 129 (80), 108 (45) and 73 (90%).

Attempted synthesis of KC(SiMe$_3$)$_2$(SiMe$_2$PPh$_2$). A slurry of KOBu^t (0.45 g, 4.02 mmol) and compound **III** (1.63 g, 4.05 mmol) in thf (20 cm^3) was treated with a solution of LiMe (4.02 mmol) in thf (10 cm^3). Gas was evolved immediately. The orange solution was stirred for 14 h, the solvent removed, and the sticky residue washed with hexane (2 × 20 cm^3) then extracted with hot toluene (30 cm^3, 50 °C). The extract was filtered and the filtrate cooled to give orange crystals, which were identified as KPPh$_2$ **6**, by an X-ray study.

Crystallography

For compounds **1**, **2**, **III** and **4**, data were collected on an Enraf Nonius CAD4 diffractometer and the structures solved by direct methods (SHELXS 86) and refined by full matrix least squares (SHELXL 93).[33] Data for structure **6** were collected on a KappaCCD instrument and refinement was by SHELXL 97.[33] All non-hydrogen atoms were anisotropic; hydrogen atom positions were refined in riding mode for **1**, **III** and Ph and CH$_2$ groups of **2**. For **1** one C$_6$H$_6$ solvate molecule was on an inversion centre and the other was at a general position and disordered; it was modelled as two rigid bodies with isotropic C atoms in slightly different orientations in the ratio 0.57 : 0.43. The Me groups were fixed at idealised geometry but the torsion angles defining the H atom positions were refined. The H attached to C(10) in **2** and all those in **4** were freely refined. In **6** a poorly defined molecule of toluene was disordered about an

Table 3 Summary of crystallographic data for compounds **1**, **2**, **III**, **4** and **6**

	1·1.5C_6H_6	**2**	**III**	**4**	**6**
Chemical formula	$C_{46}H_{54}LiPSi_3 \cdot 1.5C_6H_6$	$C_{34}H_{59}Li_2O_3PSi_3$	$C_{21}H_{35}PSi_3$	$C_{21}H_{34}NaPSi_3$	$C_{12}H_{10}KP \cdot \frac{1}{14}C_7H_8$
Formula weight	908.2	644.9	402.7	424.7	230.85
T/K	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_12_12_1$ (no. 19)	$P2_1/c$ (no. 14)
a/Å	13.967(3)	11.095(6)	6.852(2)	10.770(2)	15.1313(2)
b/Å	13.981(2)	11.356(3)	19.404(7)	13.683(2)	13.7513(2)
c/Å	16.707(5)	17.505(5)	18.012(7)	16.542(4)	39.8676(6)
α/°	67.62(2)	93.19(2)			
β/°	65.41(2)	91.03(3)	94.31(2)		94.851(1)
γ/°	60.03(1)	118.29(4)			
U/Å^3	2507(1)	1937(1)	2388(1)	2438(1)	8266(1)
Z	2	2	4	4	28
μ/mm^{-1}	0.23	0.19	0.27	0.28	0.55
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.071, 0.116	0.061, 0.130	0.049, 0.098	0.049, 0.096	0.055, 0.140
all data	0.148, 0.145	0.108, 0.152	0.085, 0.115	0.076, 0.109	0.094, 0.163
Measured/independent reflections (R_{int})	6125/6125	5383/5383	4555/4190 (0.0399)	4699/4284 (0.0400)	41955/14434 (0.060)
Reflections with $I > 2\sigma(I)$	3424	3570	2940	3347	9528

inversion centre; the Me groups were not located. Further details are given in Table 3.

CCDC reference number 186/1976.

See http://www.rsc.org/suppdata/dt/b0/b002488k/ for crystallographic files in .cif format.

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